

Fluxes of ammonia and sulfate over maize using relaxed eddy accumulation

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Abstract

The dry deposition of fine aerosol sulfate and ammonia was measured over maize using the relaxed eddy accumulation method (REA). This micrometeorological method determines the flux by sampling the concentrations in the “updraft” and “downdraft” eddy motions, with the flux being proportional to the difference in concentration between the “up” and “down” concentrations. The fine aerosol fraction and gas phase components were separated using annular denuders followed by filterpacks using Teflon filters. Measurements were made when the leaf area index was low (~ 1) and later when the canopy was fully developed ($\text{LAI} \sim 4$) to evaluate the role of LAI on the aerosol deposition velocity. The deposition measurements of sulfate aerosol yielded daytime deposition velocities larger than expected ($\sim 2 \text{ cm s}^{-1}$) from short crops but consistent with other field measurements over forests. Over a young fertilized stand of maize with a leaf area index of ~ 1 , large emissions of ammonia were observed for several days following the surface application of urea containing fertilizer. Measurements over a fully developed canopy with a leaf area index of about 4, showed both deposition and emission events.

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1. Introduction

The impact of dry deposition of sulfur and nitrogen compounds continues to be an important issue with regard to nutrient cycling and acid deposition. Improvements in the parameterizations for aerosol deposition have proceeded at a slower pace than for gas phase compounds. Advances in the measurement technology for gas phase sulfur (Benner and Stedman, 1994) and nitrogen compounds (Fehsenfeld et al., 1998) have advanced the

understanding and parameterization of their air–surface exchange. Although there have been some breakthroughs in the measurement of speciated aerosols (Herring and Stolzenburg, 1998; Weber et al., 2001), more uncertainties exist for aerosol since many of the measurement methods are not well suited for flux measurements using micrometeorological methods (Wesely and Hicks, 2000). Experiments conducted in the early 1980s (Wesely et al., 1985; Fowler, 1978) still form the basis for parameterizations (Wesely, 1989; Meyers et al., 1998; Erisman and Baldocchi, 1994) that are used to compute the annual loadings of sulfur and nitrogen in dry deposition monitoring networks in the North America (Holland et al., 1999; Meyers et al., 1991; Brook et al., 1999), South Africa (Zunckel, 1999), and in Europe (Erisman and Baldocchi, 1994; Smith et al., 2000). Measurements have

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indicated that deposition velocities for aerosols are a function of the friction velocity, implying some dependency on the leaf area index which controls, in part, the aerodynamic roughness of the canopy (Shaw and Periera, 1982).

Gas phase components of sulfur and nitrogen, in most circumstances, dominate the dry deposition relative to their aerosol counterpart. However, there are some circumstances in which the aerosol components are thought to play a significant role, such as in coastal ecosystems (Hinga et al., 1991) including Chesapeake (Larsen et al., 2001) and Tampa Bay (Poor et al., 2001). Improvements in aerosol measurement technology has been applied recently in experiments to evaluate aerosol deposition processes in Europe, where atmospheric concentrations of gas- and aerosol-phase nitrogen can be large and loadings have been determined to be a significant contribution of the total annual nitrogen input (Fournier et al., 2004). Some of these experiments have also suggested that fine aerosol deposition velocities (aerosols with diameters $<2.5 \mu\text{m}$) are greater than those currently used in many dry deposition models (Gallagher et al., 2002).

The relaxed eddy accumulation method (Businger and Oncley, 1989) or REA, a recent adaptation of the more commonly known eddy accumulation method, is a micrometeorological technique that can be used to measure the air–surface exchange of scalars. Some of the current methodologies for measuring the concentrations of gas- and aerosol-phase nitrogen and sulfur compounds are based on accumulation devices such as annular denuders and filterpacks, in which concentrations can be measured very accurately. The attractiveness of the REA method is that it can be applied to chemical species for which fast response instrumentation is not yet available, but for which other methods can be used to determine the trace species concentrations to high degree of accuracy (Guenther et al., 1996; Bowling et al., 1999). More recently, REA methods have been applied to assess the air–surface exchange of ammonia over grass (Nemitz et al., 2001) and the volatilization over a young stand of maize that was fertilized with urea (Zhu et al., 2000). To further improve the understanding of aerosol deposition processes, we combined the REA method with annular denuder/filterpack measurement systems to evaluate the sulfate deposition velocity over maize at two stages of canopy development. In the first case, measurements were conducted when the leaf area index was ~ 1 . In the second experiment, measurements were conducted over a fully grown maize canopy in order to evaluate the impact of leaf area index on the deposition velocity of aerosols $<2.5 \mu\text{m}$ diameter.

2. Methodology

2.1. Relaxed eddy accumulation

The REA method was employed to derive the fluxes of sulfate aerosol because it is well suited for accumulation devices such as filterpacks. First introduced by Businger and Oncley (1989), the REA method is a modified version of the eddy accumulation technique with the exception that sampling for concentrations in the “up” and “down” draft collectors is not proportional to the vertical wind velocity (w). Air samples are accumulated at a constant rate, in either “updrafts” ($+w$) or “downdrafts” ($-w$), which is determined by the 3D sonic anemometer used for the eddy covariance of heat, water and CO exchange. Fluxes over the sampling interval in which the air is sampled through up and down denuders and filterpacks are determined as

$$F = \beta \sigma_w (C_u - C_d) \quad (1)$$

where σ_w is the standard deviation of the vertical wind velocity, C_u and C_d the average concentrations of sulfate in the “updraft” and “downdraft” accumulators, respectively, and β is a proportionality constant that is ≈ 0.6 (Baker et al., 1992; Baker, 2000). A vertical velocity “deadband” (δ) symmetric about zero is often used in which airflow is diverted from both the up or down accumulators when $|w| < \delta$. The use of a deadband increases the concentration difference between the up and down samplers (Bowling et al., 1999) for a given flux because only the large eddies are sampled. For this study, we used a deadband of 0.05 m s^{-1} . The switching frequency between the “up”, “down”, and deadband samples was 1 s. During the first study, the instantaneous value of w at the 1 s intervals was used to govern the switching. In the second study, a filtered w with a 0.5 s time constant was used. As will be discussed later, this had some effect on the computed values of β . To compute the most appropriate value of β for the computation of the flux from Eq. (1), the air temperature and water vapor signals from the eddy covariance system were “synthetically” sampled at the same 1 s switching intervals used for the “up” and “down” aerosol sampling systems. From these measurements, β was explicitly determined using these “up” and “down” averages of temperature and water vapor, the measured σ_w , and the measured eddy covariance for heat and latent energy flux obtained during the REA sampling interval.

The fluxes of sensible and latent heat, along with the CO₂ flux was determined with the eddy covariance method. The flux was computed as

$$F_s = \overline{w's'} \quad (2)$$

where w is the vertical velocity and s is the concentration of the scalar of interest. The primes in Eq. (2) denote a departure from a temporal average (i.e. $w' = w - \bar{w}$) and the overbar represents an averaging time. Sampling was done at 10 Hz and average eddy covariance fluxes were determined at 30 min intervals. The deviations from the mean were determined using a digital high pass recursive filter (McMillen, 1988). After initialization, the real-time running mean (χ) at each sample interval was computed as

$$\chi_i = \alpha\chi_{i-1} + (1 - \alpha)\chi \quad (3)$$

where χ_i is the current running mean, χ_{i-1} is the running mean from the previous time step, and χ is the current instantaneous value. The value α is a constant that results from the sampling interval (Δt) and desired time constant τ as

$$\alpha = \exp(-\Delta t/\tau) \quad (4)$$

We used a value of 400 s for τ which has been considered appropriate for short vegetation (Shuttleworth, 1988).

2.2. Site description

Two separate experiments were conducted at the United States Department of Agriculture (USDA) Beltsville Agricultural Research Center (BARC) near Beltsville, Maryland (MD). The site was in the center of a slightly undulating 15 hectare (ha) maize field with a fetch of at least 100 m in all directions. The maize cultivar ‘Pioneer 33J56’ was planted on 12 May with a final population of approximately 55,000 plants ha⁻¹. The first experiment began on 12 June 2001 and samples were taken for 3 days. Samples were collected twice each day and represented a 4 h morning exposure followed by a 4 h afternoon exposure. No samples were collected at night. The maize crop was about 20–50 cm tall during the first experiment with a leaf area index (LAI) of 1. A sidedress application of urea–ammonium–nitrate (UAN) was applied at a rate of 105 kg N ha⁻¹ and contained 50% of its N as urea-N, 25% as ammonium-N and 25% as nitrate-N. The fertilizer was applied as a shallow sub-surface band, using a disk opener followed by a shallow injection knife which targeted the application to a 2 cm deep band mid-way between the rows of maize. Visual inspection of the application zones revealed that about 25% of the

UAN was not completely incorporated due to stones, topographic undulation, and limited flexibility of a wide tractor mounted tool bar. Ammonia volatilization would therefore be expected to be substantially reduced due to soil incorporation, compared to a surface broadcast application, but would not be totally eliminated.

The second phase of the experiment began on 26 July in the same maize field and continued for about 30 days. No fertilization or other management practices were conducted on the maize crop during this experiment. The REA samples were collected after 4 h exposures during the morning or afternoon periods, with occasional samples collected during the evening. The maize canopy was fully developed with a height of 2.8 m and a leaf area index of 4.

2.3. Filterpack sampling and chemical analysis

Three single-stage denuder/dual stage filter pack (FP) assemblies (URG Corp., Carrboro, NC) were affixed to a sampling mast near, but below the level of the sonic anemometer to measure ammonia and particulate sulfate in updrafts, downdrafts, and “deadband” flows as determined from the sonic anemometer. Ambient air flow through the denuder/filterpack assemblies was provided by a Gast diaphragm pump, metered with a common mass flow controller (Sierra Corp) or ball flow meter (second phase of the experiment). Total flow through each denuder/filterpack system was measured with a dry gas meter (Schlumberger Gallus, 2000). A fourth, independent denuder assembly was sampled concurrently with the REA denuders for each sampling interval, using an identical flow rate and separate gas handling pneumatics and metering devices. This system provided a quality control check of the data, as the sum of the loadings on the REA denuder and filterpack systems was compared to that on the continuous system for each sampling run. Prior to and after the two field studies, the four dry gas meters were plumbed in series and the total flow through each was compared. The coefficient of variation (σ/\bar{x}) was 0.67%, and the mean flow rate (calculated from the average total flow divided by sampling time) agreed to within 2.8% of the flow as simultaneously measured with a primary flow calibrator (Gilian Corp.). Similar tests in 1999 yielded a CV of 0.43%, and an agreement within 2.6% of the primary flow standard.

Each denuder/filterpack assembly consisted of a cyclone separator to exclude particles larger than 2.5 μ m at a flow rate of 10 l per minute; an annular denuder coated with a 1% solution of citric acid (citric acid monohydrate, Fisher Scientific) in a 50/50 water/

methanol matrix; and a 2-stage filter pack consisting of a PTFE membrane (1 μm pore Zefluor membrane, Gelman) and backup cellulose filter (Whatman 41) impregnated with 0.1 M oxalic acid in 85/15 methanol/glycerol. A field blank system, composed of a denuder and 2-stage filter pack (FP), but without a cyclone separator, was deployed along with the switched and continuous denuders for the duration of each sampling interval. No ambient air was pulled through the blank system. Side-by-side deployments of the samplers in the laboratory prior to the start of the study yielded a precision ($\text{CV} = \sigma/\bar{x}$) of measured gas-phase NH_3 of 1.5–3.7%, including all calibration, sampling, and flow rate calculations.

The denuders were washed thoroughly with triple rinses and vigorous shaking in 18 M Ω deionized (DI) water, and coated with 10 ml of the citric acid solution. The excess coating solution was decanted, and the denuders were dried on a manifold with compressed ultra high pure air (Air Products, Bladensburg, MD). Denuders were coated immediately prior to sampling to prevent blank contamination. All components of the filter pack assemblies were sonicated in DI water and allowed to dry well before the start of the sampling period. PTFE membranes were installed in the first FP stage. Pre-washed/vacuum dried Whatman 41 filters were dipped into the oxalic acid impregnating solution, shaken of excess solution, and placed wet into the second stage of the FP assembly. Cyclone separators were cleaned with DI water and methanol and dried immediately prior to deployment. The denuder assemblies were assembled and then transported to the USDA site. During the first phase of the study (June 2001) all sample manipulation, preparation, and extraction was performed with gloved hands in the NOAA/Air Resources laboratories in Silver Spring, MD, some 16 km from the USDA site. During the second phase of REA research (July–August 2001), all sample manipulation was performed in the USDA/ BARC laboratory, 500 m from the tower. Ambient air was pulled through a weak phosphoric acid solution to provide ammonia-free air to a clean hood in which the manipulations were performed.

After sampling, denuders were extracted with one 20-ml rinse of 18 M Ω deionized DI water from a re-pipet dispenser (MFR), and the extract poured into clean hi-density polyethylene (HDPE) scintillation vials (Fisher Scientific). The impregnated filters were removed from the FP assemblies and placed into scintillation vials, extracted with 20 ml DI water, and sonicated for 30 min. Teflon prefilters were extracted with a mixture of 90/10 water/methanol and sonicated. All extracts were stored at 4 $^{\circ}\text{C}$ until analysis with the

ion chromatograph. The volume of water or water/methanol dispensed by the re-pipet was determined by weighing repeated aliquots from the dispenser.

Denuder and filter extracts were analyzed for NH_4^+ using a Dionex DX-300 ion chromatograph (IC). Fifteen millimolars of methanesulfonic acid was used as the system eluent at a flow rate of 1.20 ml/min; DI water was used as the regenerent for the electronic suppressor operating in the external water mode. The IC was operated with a 100 μl sample loop and was calibrated with aqueous standards from 1 to 200 M to thoroughly characterize the non-linear system response to NH_4^+ . All denuder and filter extracts were reanalyzed at least once, and the average measured NH_4^+ was reported. Five milliliters auto-sampler vials, equipped with filtered caps (Dionex Corp., Sunnyvale, CA) were used to contain the sample aliquots. Denuder extracts containing more than 200 M NH_4^+ were diluted with deionized water and reanalyzed, so that their concentrations could be interpolated from the non-linear calibration curves. Filter and denuder extracts containing high loadings of Na^+ were reanalyzed using a 25 μl sample loop to increase the separation between the adjacent Na^+ and NH_4^+ peaks.

Filter extracts were analyzed for SO_4^{2-} using a Dionex model DX-120 ion chromatograph fitted with a AS9-HC analytical column, an AG9-HC guard column and either a 100 μl or 200 μl sample loop. The eluent was 12 mM Na_2CO_3 while the suppressor operated in the self regenerating mode. Sulfate standards were made up in 10% methanol and 18 M Ω DI water to match the filterpack extracting solutions. Sulfate standards for the 100 μl loop ranged from 0.5 to 111 μM .

3. Results

3.1. Measured aerosol deposition velocities and NH_3 exchange for low LAI

The meteorological conditions were similar during the 3-day experimental period beginning on Day 163 (Fig. 1). Wind speeds displayed a diurnal cycle with midday values between 2 and 3 m s $^{-1}$ at a height of 3 m. Air temperature and relative humidity were also very consistent for the 3-day period. Daily high temperatures peaked around 32 $^{\circ}\text{C}$ with nighttime minima bottoming out around 17 $^{\circ}\text{C}$. High humidities (>95%) were observed each evening with daytime minima near 50%. All 3 days were partly to mostly sunny with solar radiation values exceeding 800 W m $^{-2}$ each of the 3 days. The nearly constant meteorological conditions were also reflected in the narrow range observed for σ_w

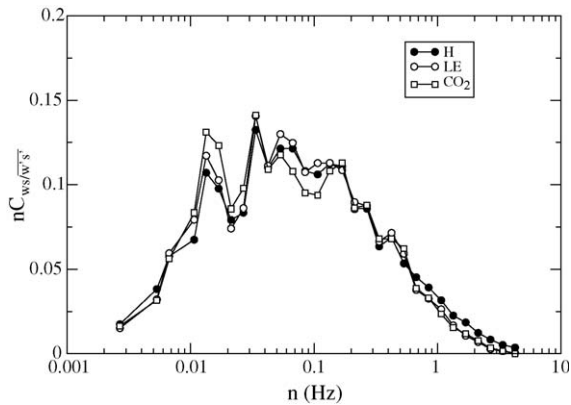


Fig. 1. Co-spectra of normalized fluxes of sensible, latent and carbon dioxide.

measured during each of the REA runs (Table 1). The REA constant of proportionality derived from the heat flux ($\beta(\theta)$) also showed a narrow range over the 3 days. The average of the calculated values of $\beta(\theta)$ in the first experiment was 0.63 and is consistent with those reported by Nemitz et al. (2001) using a similar strategy to derive a value for β from measurements of temperature gradients and fluxes derived from eddy covariance. The effect of using a 1 s switching frequency for the REA valve control on the potential loss of flux at higher frequencies was investigated by examining the normalized co-spectra for heat, water and CO_2 flux (Fig. 1). The co-spectral estimates were derived from six 30 min segments of 10 Hz data from DOY 164. From this graph, 5% of co-spectral area for sensible heat, and 3% for water vapor and CO_2 were at frequencies greater than 1 Hz (Fig. 2).

Concentrations of sulfate were greatest on Days 163 and 164 and ranged between 5 and $7 \mu\text{g m}^{-3}$. On DOY 165, sulfate concentrations were roughly 50% of those observed during the preceding 2 days (Table 1). Wind directions during the first 2 days ranged from 100° to 200° , transporting to the site air influenced by the Washington, DC metropolitan

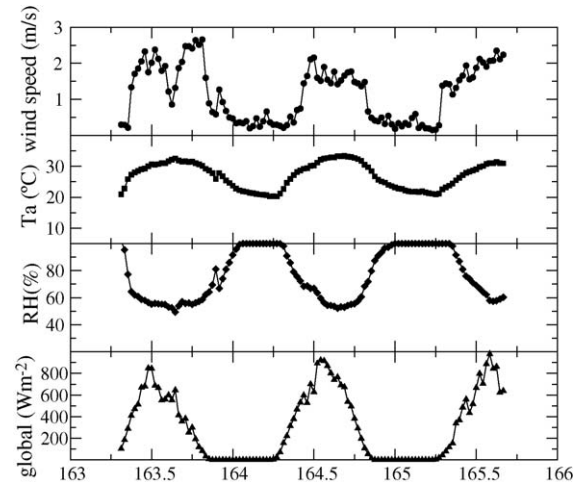


Fig. 2. Meteorological conditions during first experiment over recently fertilized maize canopy.

corridor. On DOY 165, easterly winds prevailed which have more coastal air mass characteristics. For all 3 days of sampling, the average daytime sulfate deposition rate was $-0.108 \pm 0.036 \mu\text{g m}^{-2} \text{s}^{-1}$ with an average concentration of $5.2 \mu\text{g m}^{-3}$. Combining the average sulfate concentration and deposition rate yields a deposition velocity (v_d) $\approx 2 \text{ cm s}^{-1}$ for the six REA runs during the low LAI period from DOY 163–165. The concentrations of NH_3 increased from $16 \mu\text{g m}^{-3}$ at the beginning of the measurement period on Day 163 to over $40 \mu\text{g m}^{-3}$ on DOY 165. Note that the sampling site was in the middle of the field so winds from any direction would have the same influence of the concentrations if the emission rates had little variation spatially. Corresponding NH_3 fluxes also increased from a daily average emission rate of $0.6\text{--}2 \mu\text{g m}^{-3} \text{s}^{-1}$ on DOY 165 (Fig. 3). The difference between the up and downdraft denuders was greatest on DOY 164 even though the levels of turbulent mixing as depicted by σ_w showed little day-to-day variation.

Table 1

Micrometeorological relaxed eddy accumulation parameters including sulfate concentrations, standard deviation of the vertical wind velocity (σ_w), friction velocity (u^*), and flux constant of proportionality computed from sensible heat flux ($\beta(\theta)$)

Day	$C_u(\text{SO}_4^{2-})$ ($\mu\text{g m}^{-3}$)	$C_d(\text{SO}_4^{2-})$ ($\mu\text{g m}^{-3}$)	$C_u(\text{NH}_3)$ ($\mu\text{g m}^{-3}$)	$C_d(\text{NH}_3)$ ($\mu\text{g m}^{-3}$)	σ_w (m s^{-1})	$\beta(\theta)$	Flux SO_4^{2-} ($\mu\text{g m}^{-2} \text{s}^{-1}$)	Flux NH_3 ($\mu\text{g m}^{-2} \text{s}^{-1}$)
163	6.52	6.21	16.27	12.57	0.33	0.67	0.067	0.821
163	6.16	7.12	16.30	13.67	0.29	0.61	-0.169	0.463
164	5.41	5.98	33.63	20.73	0.27	0.58	-0.092	2.051
164	6.43	7.54	41.79	27.51	0.29	0.64	-0.205	2.652
165	2.87	3.36	48.42	38.65	0.29	0.66	-0.094	1.895
165	1.99	2.61	47.51	39.48	0.36	0.70	-0.153	2.016

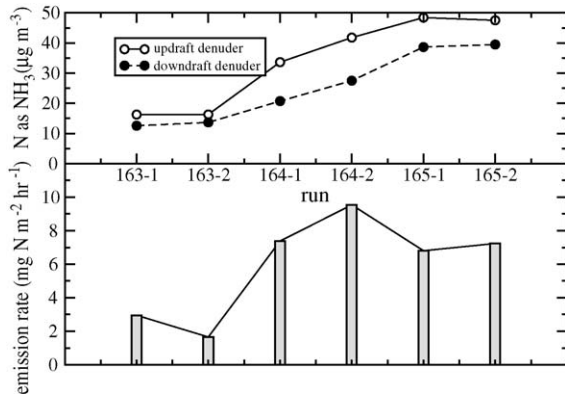


Fig. 3. Ammonia concentrations and fluxes (emission rates) during first experiment over small maize crop.

3.2. Measured sulfate deposition velocities and NH_3 exchange for full canopy

During the second phase of the experiment from DOY 205 to 240, 20 REA runs were conducted. The range in sulfate concentrations was similar to those observed during the first experiment, but were in general lower. The highest concentrations were observed during the last 6 REA runs (Table 2). The measured sulfate exchange rate showed deposition to the surface in 19 of the 20 REA runs. A positive

flux (away from the surface) was observed during the morning run on DOY 209. This was also one of the days with the lowest observed concentration of sulfate aerosol. The level of vertical turbulent mixing as depicted by the average σ_w for each REA run was expectedly higher given the fully developed nature of the maize canopy. The values of β were lower in the second experiment since a deadband of 0.1 m s^{-1} was used but are consistent with the β model of Pattey et al. (1993) that was evaluated by Katul et al. (1996) in an assessment of the REA method to estimate fluxes of trace gases. The average daytime sulfate deposition rate for the second phase of the experiment was $-0.122 \pm 0.031 \mu\text{g m}^{-2} \text{ s}^{-1}$ at an average concentration of $3.8 \mu\text{g m}^{-3}$. Combining the average sulfate concentration and deposition rate, yields a deposition velocity (v_d) $\approx 3 \text{ cm s}^{-1}$ for the 20 REA runs conducted over the fully developed maize canopy.

The NH_3 concentrations and fluxes observed during the second phase of REA experiments were much lower than those observed earlier. Several of the early runs were below the detectable limit. Ambient concentrations of NH_3 for the remaining of the REA experiments were all $< 6 \mu\text{g m}^{-3}$ with nearly 50% of the concentrations $< 2 \mu\text{g m}^{-3}$. Both emission and deposition events were observed with fluxes ranging from -0.2 to $0.13 \mu\text{g m}^{-2} \text{ s}^{-1}$.

Table 2

Micrometeorological relaxed eddy accumulation parameters including sulfate concentrations, standard deviation of the vertical wind velocity (σ_w), and flux constant of proportionality computed from sensible heat flux ($\beta(\theta)$)

Day	$C_u(\text{SO}_4^{2-})$ ($\mu\text{g m}^{-3}$)	$C_d(\text{SO}_4^{2-})$ ($\mu\text{g m}^{-3}$)	$C_u(\text{NH}_3)$ ($\mu\text{g m}^{-3}$)	$C_d(\text{NH}_3)$ ($\mu\text{g m}^{-3}$)	σ_w (m s^{-1})	$\beta(\theta)$	$V_{d,\text{max}}$ (cm s^{-1})	Flux SO_4^{2-} ($\mu\text{g m}^{-2} \text{ s}^{-1}$)	Flux NH_3 ($\mu\text{g m}^{-2} \text{ s}^{-1}$)
205	1.90	2.18	1.29	1.13	0.46	0.44	9.8	-0.055	0.033
206	1.44	1.88	—	—	0.36	0.98	8.6	-0.094	—
206	2.33	2.52	—	—	0.66	0.67	10.5	-0.074	—
206	1.49	1.56	—	—	0.59	0.65	14.9	-0.024	—
208	0.48	0.51	—	—	0.47	0.56	10.5	-0.009	—
208	1.06	1.09	2.72	2.71	0.38	0.49	9.9	-0.007	0.001
209	0.64	0.58	2.73	2.53	0.39	0.51	12.2	0.014	0.040
209	0.86	0.94	1.70	1.48	0.46	0.53	9.8	-0.020	0.052
211	0.50	0.66	1.26	0.75	0.37	0.52	10.2	-0.032	0.100
211	1.35	1.69	0.33	0.22	0.31	0.48	2.1	-0.051	0.017
212	0.29	0.38	1.20	0.76	0.34	0.47	7.6	-0.015	0.069
213	2.69	2.91	1.17	0.63	0.32	0.48	7.3	-0.034	0.082
214	0.91	1.13	1.13	0.64	0.45	0.58	9.4	-0.057	0.128
215	2.16	2.18	0.70	0.56	0.43	0.59	5.4	-0.004	0.035
219	5.86	7.38	1.36	2.06	0.44	0.80	8.5	-0.298	-0.171
219	7.21	7.50	2.40	2.35	0.41	0.60	9.6	-0.072	0.012
219	6.76	8.17	2.65	3.34	0.32	0.49	0.6	-0.268	-0.106
220	5.70	7.16	1.80	1.94	0.42	0.32	8.0	-0.371	-0.019
220	7.70	8.75	4.42	5.19	0.49	0.54	7.4	-0.310	-0.203
240	5.01	5.49	2.23	2.01	0.42	0.51	16.1	-0.121	0.048

4. Discussion

4.1. Sulfate deposition

The computed deposition velocities for sulfate are larger than most current parameterizations used in air quality networks and deposition routines in regional scale deposition models (Wesely et al., 1985). However, large measured values for aerosol deposition velocities have been reported over several types of surfaces. In a comprehensive experiment conducted over Douglas fir in the Netherlands, Erisman et al. (1997) reported larger than expected deposition velocities for sulfate with maximum values of approximately 4 cm s^{-1} for unstable conditions. Over grassland, Everett et al. (1979) reported sulfate deposition velocities that were on the order 2 cm s^{-1} for unstable conditions. Similarly, Sievering (1986) reported large deposition velocities for sulfate during high wind conditions using the gradient method. Using a mass balance method, Horvath (2003) derived average deposition velocities for ammonium sulfate that were in excess of 0.8 cm s^{-1} . Using a gradient method over alfalfa, Dabney and Boudin (1990) measured deposition velocities for ammonium that were on average 2 cm s^{-1} . Leaf pubescence or leaf “hairiness” was suggested by Chamberlain (1967) as a major mechanism contributing to the capture of particles of less than $5 \mu\text{m}$. Later work by Fleisher and Parungo (1974) and Martell (1974) supported this conclusion by demonstrating factors of 10 increase in deposition rates of particles to leaves with pubescence versus those with more smooth and waxy surfaces. In a recent analysis, Reynolds (2000) using Lagrangian stochastic models, showed that particle deposition of micron and sub-micron particles is extremely sensitive to the micro-roughness of the surface. Leaves of maize are generally not smooth but are considered aerodynamically rough compared to leaves of deciduous and conifer forests. The level of pubescence or trichome density is a morphological characteristic in crops that is controlled genetically and has been shown to be important in the defense of insect predators (Levin, 1973). The conclusions reached in a 1983 review of deposition processes (NRCS, 1983), that was recently reiterated by Wesely and Hicks (2000) and Garland (2001) concur that there remains considerable disagreement between models and field measurements of particulate fluxes, especially those associated with sulfate and nitrate.

4.2. Air–surface exchange of NH_3

The air–surface exchange of NH_3 is complicated by the fact that both the vegetation and soil can act as a sink

or source of NH_3 . Emissions can occur at the soil surface and thru leaf stomata while at the same time deposition to the leaf cuticle, stems and other vegetative is ongoing. During the first experiment, the NH_3 exchange was dominated by emission from the recently fertilized field (Table 1). Gaseous loss by NH_3 volatilization is governed by many factors that can be grouped into atmospheric conditions, soil factors, and management practices. Atmospheric conditions include temperature, wind speed, relative humidity, and atmospheric turbulence. Soil factors include soil pH and buffering capacity, surface temperature and moisture content, surface residues and roughness, and urease activity. Management practices include the type of nitrogen fertilizer and the fertilizer application method. The ammonia emissions in Table 1 show a small emission on DOY 163 followed by larger emissions the next 2 days. The time lag in NH_3 emissions is typical for urea sources undergoing hydrolysis, as observed by Ferguson et al. (1987) for UAN solutions and by McInnes et al. (1986b) for urea solutions. The larger fluxes of about $2 \mu\text{g N m}^{-2} \text{ s}^{-1}$ over the next 2 days are also consistent with other data in the literature. For example, Ferguson et al. (1987) summarized data from a micrometeorological mass balance study by McInnes et al. (1986a) that reported an average ammonia flux of $2.8 \mu\text{g N m}^{-2} \text{ s}^{-1}$ over 5 days following a surface application of 200 kg N ha^{-1} of UAN to wheat straw residues under dry conditions in Kansas before irrigation or rainfall. These moderate fluxes under dry conditions increased substantially after rainfall or irrigation (McInnes et al., 1986a) to fluxes commonly ranging from 4 to $12 \mu\text{g N m}^{-2} \text{ s}^{-1}$. In a second UAN study, McInnes et al. (1986b), substantially larger fluxes of 5 to $>40 \mu\text{g N m}^{-2} \text{ s}^{-1}$ were reported, with losses closely following small irrigation events. The total nitrogen losses reported in these two studies amounted to 8 and 17%, respectively, of the total N applied as UAN. Similar ammonia fluxes have been reported from applications of urea fertilizer, which is the primary source of NH_3 in UAN solutions. For example, McInnes et al. (1986b) reported ammonia fluxes of 1– $4 \mu\text{g N m}^{-2} \text{ s}^{-1}$ from bare soil following the application of 120 kg N ha^{-1} of urea solution, while Wilson et al. (1983) reported ammonia fluxes of 1– $10 \mu\text{g N m}^{-2} \text{ s}^{-1}$ from urea fertilizer applied to a short grass pasture surface. In a more recent study using REA to assess ammonia losses, Zhu et al. (2000) measured peak losses close to $1 \mu\text{g N m}^{-2} \text{ s}^{-1}$ over a young maize field that was fertilized with a broadcast application of urea at a rate of 138 kg N ha^{-1} . During their 23 days of measurements, about 0.8% of the

applied urea was volatilized. The average ammonia flux of $1.65 \mu\text{g N m}^{-2} \text{s}^{-1}$ reported in Table 1 is consistent with the findings of Zhu et al. (2000) and with other literature values, with our somewhat lower emissions attributed to the partial incorporation of the UAN by shallow injection. The estimated total loss of the $\text{NH}_3\text{-N}$ in the first experiment, assuming negligible losses at night and 50% of the average rate during the non-sampled 7 h of daylight, amounts to 0.7 kg N ha^{-1} , which is slightly less than 1% of the total applied nitrogen. These losses would be larger had observations been extended beyond Day 165, but because a 38 mm rainfall occurred on Day 167 (which would quench losses), the total NH_3 loss would have likely amounted to less than 2% of the applied nitrogen.

In the absence of a strong soil surface emission, the air–surface exchange of NH_3 is a complicated process that is driven by many factors including surface wetness, stomatal conductance, ambient concentrations, and antecedent dry deposition of other atmospheric pollutants. On average, it appears that vegetation and atmospheric NH_3 are in equilibrium such that if the atmospheric concentration is above a critical threshold, deposition occurs and if the concentration is below this “apparent” compensation point, emission occurs. This view of ammonia exchange is limited to circumstances in which the soil does not play a significant role as either a source or sink of NH_3 . For understanding and modeling NH_3 exchange in agricultural systems, it becomes necessary to quantify the emission from the soil surface as well as accounting for the temperature dependency of leaf compensation points (Nemitz et al., 2000) that are now part of models used to predict bi-directional fluxes (Sutton et al., 1998). Stomatal compensation points for NH_3 in agricultural systems have been shown to vary from 0 to $4 \mu\text{g m}^{-3}$ (Mattsson and Schjoerring, 2002; Yamulki and Harrison, 1996; Ross and Jarvis, 2001). At first glance (Table 2), the measurements during the second experiment, when the canopy was fully developed, show no consistent pattern with both emission and deposition events occurring. However, when the NH_3 fluxes are plotted against the ambient concentrations (Fig. 4), a somewhat more coherent picture begins to emerge. The bulk of NH_3 fluxes at low ambient concentrations ($<2 \mu\text{g m}^{-3}$) are dominated by emission events whereas the fluxes at higher concentrations generally show uptake of NH_3 . The NH_3 compensation point depends on many factors (Schjoerring et al., 1998), such as leaf age, plant water stress and the availability of nitrogen in the root zone (Mattsson and Schjoerring, 2002). Techniques to determine the

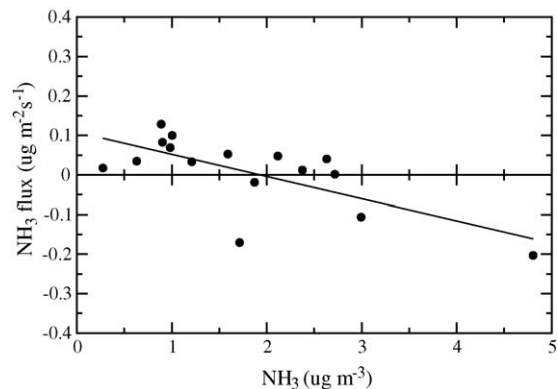


Fig. 4. NH_3 flux plotted against concentration during second phase of experiment.

apoplastic concentrations of H^+ and NH_4^+ were not applied in this study.

To assess the possible range of stomatal compensation points, a multi-layer plant canopy model, that is capable of treating the multi-level sources/sinks of NH_3 was utilized. The model has been shown to adequately predict profiles of the mean wind speed, air temperature and humidity (Meyers and Paw, 1986), HNO_3 (Meyers et al., 1989), and O_3 (Finkelstein et al., 2004), within and above plant canopies. The transfer coefficient at the soil–air interface (used to estimate the ammonia emission at the soil surface) was predicted using the model described by Sauer and Norman (1995). The leaf cuticular resistance for ammonia was assumed to be minimal (10 s m^{-1}). By minimizing the overall squared error from the measured flux during the second study, a

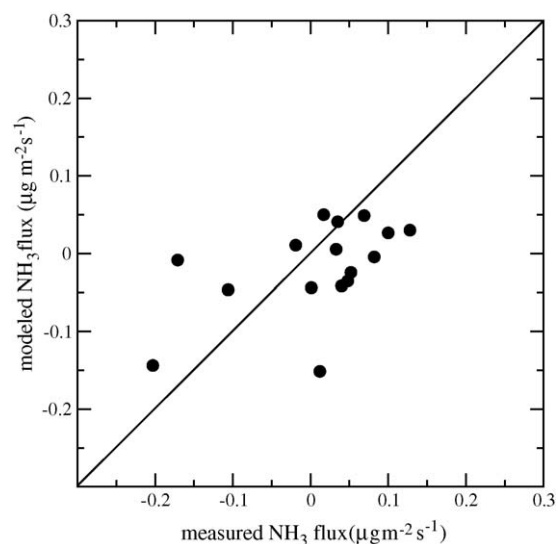


Fig. 5. Modeled and measured exchange of ammonia assuming a compensation point of $6 \mu\text{g m}^{-3}$.

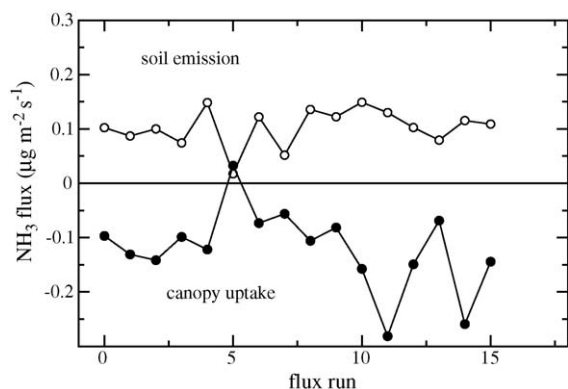


Fig. 6. Balance between the modeled emission of ammonia at the soil surface and the modeled uptake of ammonia by the maize canopy (both cuticular and stomatal) for each of the REA runs during the second experiment.

stomatal compensation point of $6 \mu\text{g NH}_3 \text{ m}^{-3}$ produced the overall results (Fig. 5), although the difference in results from using a compensation point of $2 \mu\text{g NH}_3 \text{ m}^{-3}$ were not significantly different. The net ammonia flux above the maize canopy resulted from the difference between NH_3 emission from the soil surface and uptake by the canopy which consists of deposition to both the leaf cuticle and stomatal diffusion (Fig. 6). On average, the magnitude of modeled uptake by the canopy was 20% more than the emission of ammonia from the soil surface. The complex interaction between the sources and sinks within an agricultural ecosystem require detail observations of ammonium levels in the soil, airspace in the canopy, ambient levels above the canopy and the concentrations of ammonium in the apoplast of the leaf tissue.

5. Conclusion

The relaxed eddy accumulation method was used to determine the air–surface exchange of NH_3 and aerosol sulfate over a recently fertilized young stand of maize ($\text{LAI} \sim 1$) and later over the fully developed stand. Measurements of sulfate deposition rates yield higher deposition velocities than are predicted from models, but which are consistent with results from other field experiments. The average sulfate deposition velocities (v_d) were 2 and 3 cm s^{-1} for the low and fully developed maize canopies, respectively. Leaf pubescence is thought to play a major role in particle removal.

Ambient ammonia concentrations were substantially increased for several days after application of liquid urea–ammonium–nitrate fertilizer. Significant ammonia emissions were observed for several days following the fertilizer application under low LAI conditions. The

emission fluxes were consistent with other values in the literature, although they represented a small percentage of the total nitrogen applied. Measurements conducted later, with an LAI of about 4, suggest the concept of an ammonia compensation point, with deposition occurring at higher levels of ambient ammonia concentrations. However, the complex source/sinks distributions of ammonia within these agricultural ecosystem preclude the application of the deposition velocity concept. Modeled air–surface exchange of ammonia showed that nearly all of the ammonia emitted from the soil was taken up by the canopy, with some additional removal of ammonia from the atmosphere. To fully characterize the exchange of ammonia, concentrations of ammonium in the soil and leaf tissue should be measured along with the concentration of ammonia above the canopy.

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References

- Baker, J.M., 2000. Conditional sampling revisited. *Agric. For. Meteorol.* 104, 59–65.
- Baker, J.M., Norman, J.M., Bland, W.L., 1992. Field scale application of flux measurement by conditional sampling. *Agric. For. Meteorol.* 62, 31–52.
- Benner, R.L., Stedman, D.H., 1994. Chemical mechanism and efficiency of the sulfur chemiluminescence detector. *Appl. Spectrosc.* 48 (7), 848–851.
- Bowling, D.R., Delancy, A.C., Turnipseed, A.A., Baldocchi, D.D., Monson, R.K., 1999. Modification of the relaxed eddy accumulation technique to maximize scalar mixing ratio differences in updrafts and downdrafts. *J. Geophys. Res.* 104 (D8), 9121–9133.
- Brook, J., Zhang, L., Franco, D., Padro, J., 1999. Description and evaluation of a model of deposition velocities for routine estimates of air pollutant dry deposition over North America. Part 1. Model development. *Atmos. Environ.* 33, 5037–5052.
- Businger, J.A., Oncley, S.P., 1989. Flux measurements with conditional sampling. *J. Atmos. Oceanic Technol.* 7, 349–352.
- Chamberlain, A.C., 1967. Transport of lycopodium spores and other small particles to rough surfaces. *Proc. Roy. Soc. London* 296, 45–70.

- Dabney, S.M., Boudin, D.R., 1990. Apparent deposition velocity and compensation point of ammonia inferred from gradient measurements above and through alfalfa. *Atmos. Environ.* 24, 2655–2666.
- Erisman, J.W., Baldocchi, D.D., 1994. Modelling dry deposition of SO₂. *Tellus B* 46, 159–171.
- Erisman, J.W., Draaijers, G., Duyzer, J., Hofschreuder, P., Van Leeuwen, N., Romer, F., Ruijgrok, W., Wyers, P., Gallagher, M., 1997. Particle deposition to forests—summary of results and applications. *Atmos. Environ.* 31 (3), 321–332.
- Everett, R.G., Hicks, B.B., Berg, W.W., Winchester, J.W., 1979. An analysis of particulate sulfur and lead gradient data collected at Argonne National Laboratory. *Atmos. Environ.* 13, 931–934.
- Fehsenfeld, F.C., Huey, G.L., Sueper, D.T., Norton, R.B., Williams, E.J., 1998. Ground-based intercomparison of nitric acid measurement techniques. *J. Geophys. Res.* 103 (D3), 3343–3353.
- Ferguson, R.B., McInnes, K.J., Kissel, D.E., Kanemasu, E.T., 1987. Comparison of methods of estimating ammonia volatilization in the field. *Fertilizer Res.* 15, 55–69.
- Finkelstein, P.L., Davison, A.W., Neufeld, H.S., Meyers, T.P., Chappelka, A.H., 2004. Sub-canopy deposition of ozone in a stand of cutleaf coneflower. *Environ. Pollut.* 131, 295–303.
- Fleisher, R.L., Parungo, F.P., 1974. Aerosol particles on tobacco trichomes. *Nature* 250, 158–159.
- Fournier, N., Dore, A.J., Vieno, M., Weston, K.J., Dragosits, U., Sutton, M.A., 2004. Modelling the deposition of atmospheric oxidised nitrogen and sulphur to the United Kingdom using a multi-layer long range transport model. *Atmos. Environ.* 38, 683–694.
- Fowler, D., 1978. The dry deposition of SO₂ on agricultural crops. *Atmos. Environ.* 12, 369–373.
- Gallagher, M.W., Nemitz, E., Dorsey, J.R., Fowler, D., Sutton, M.A., Flynn, M., Duyzer, J., 2002. Measurements and parameterizations of small aerosol deposition velocities to grassland, arable crops, and forests: influence of surface roughness length on deposition. *J. Geophys. Res.* 107 (D12).
- Garland, J., 2001. On the size dependence of particle deposition. *Water Air Soil Pollut.: Focus* 1, 323–332.
- Guenther, A., Baugh, A., Davis, K., Hampton, G., Harley, P., Klinger, L., Vierling, L., Zimmerman, P., Allwine, A., Dilts, S., Lamb, B., Westberg, H., Baldocchi, D., Geron, C., Pierce, T., 1996. Isoprene fluxes measured by enclosure, relaxed eddy accumulation, surface layer gradient, mixed layer gradient, and mixed layer mass balance. *J. Geophys. Res.* 101 (D13), 18555–18567.
- Herring, S.V., Stolzenburg, M.R., 1998. PM_{2.5}: a Fine Particle Standard. *J. Air Waste Manage. Assoc.* (Chapter: A new method for the automated high-time resolution measurement of PM_{2.5} nitrate).
- Hinga, K.R., Keller, A.A., Oviatt, C.A., 1991. Atmospheric deposition and nitrogen inputs to coastal waters. *Ambio* 20, 256–260.
- Holland, D.M., Principe, P.P., Sickles II, J.E., 1999. Trends in atmospheric sulfur and nitrogen species in the eastern United States for 1989–1995. *Atmos. Environ.* 33, 37–49.
- Horvath, L., 2003. Dry deposition velocity of ± 2.5 ammonium sulfate particles to a Norway spruce forest on the basis of s- and n-balance estimations. *Atmos. Environ.* 37, 4419–4424.
- Katul, G., Finkelstein, P.L., Clarke, J.F., Ellestad, T.G., 1996. An investigation of the conditional sampling method used to estimate fluxes of active, reactive and passive scalars. *J. Appl. Meteorol.* 35, 1835–1845.
- Larsen, R.K., Steinbacher, J.C., Baker, J., 2001. Ammonia exchange between the atmosphere and the surface waters at two locations in the Chesapeake Bay. *Environ. Sci. Technol.* 35, 4731–4738.
- Levin, D.A., 1973. The role of trichomes in plant defense. *Quart. Rev. Biol.* 48, 3–15.
- Martell, E.A., 1974. Radioactivity of tobacco trichomes and insoluble smoke particles. *Nature* 249, 215–217.
- Mattsson, M., Schjoerring, J.K., 2002. Dynamic and steady-state responses of inorganic nitrogen pools and NH₃ exchange in leaves of *Lolium perenne* and *Bromus erectus* to changes in root nitrogen supply. *Plant Physiol.* 128 (2), 742–750.
- McInnes, K.J., Ferguson, R.B., Kissel, D.E., Kanemasu, E.T., 1986a. Ammonia loss from applications of urea-ammonium nitrate solution to straw residue. *Soil Sci. Soc. Am.* 50, 969–974.
- McInnes, K.J., Ferguson, R.B., Kissel, D.E., Kanemasu, E.T., 1986b. Field measurements of ammonia loss from surface application of urea solution to bare soil. *Agron. J.* 78, 192–196.
- McMillen, R.T., 1988. An eddy correlation technique with extended applicability to non-simple terrain. *Bound.-Lay. Meteorol.* 43, 231–245.
- Meyers, T.P., Finkelstein, P.L., Clarke, J., Ellestad, T.G., Sims, P.F., 1998. A multi-layer model for inferring dry deposition using standard meteorological measurements. *J. Geophys. Res.* 103 (D17), 22645–22661.
- Meyers, T.P., Hicks, B.B., Hosker, R.P., Womack, J.D., Satterfield, L.C., 1991. Dry deposition inferential techniques. II. Seasonal and annual deposition rates of sulfur and nitrate. *Atmos. Environ.* 25, 2361–2370.
- Meyers, T.P., Huebert, B.J., Hicks, B.B., 1989. HNO₃ deposition to a deciduous forest. *Bound.-Lay. Meteorol.* 49, 395–410.
- Meyers, T.P., Paw, U.K.T., 1986. Modeling the plant canopy micro-meteorology with higher-order closure principles. *Agric. For. Meteorol.* 41, 143–163.
- Nemitz, E., Flynn, M., Williams, P.I., Milford, C., Theobald, M.R., Blatter, A., Gallagher, M.W., Sutton, M.A., 2001. A relaxed eddy accumulation system for the automated measurement of atmospheric ammonia fluxes. *Water Air Soil Pollut.: Focus* 1, 189–202.
- Nemitz, E., Sutton, M.A., Schjoerring, J.K., Husted, S., Wyers, G.P., 2000. Resistance modelling of ammonia exchange over oilseed rape. *Agric. For. Meteorol.* 105, 405–425.
- NRCS, 1983. Acid Deposition-Atmospheric Processes in North America: A Review of Current Scientific Understanding. National Academy Press, Washington, DC.
- Pattey, E., Desjardins, R.L., Rochette, P., 1993. Accuracy of the relaxed eddy-accumulation technique evaluated using CO₂ flux measurements. *Bound.-Lay. Meteorol.* 66, 341–355.
- Poor, N., Pribble, R., Greening, H., 2001. Direct wet and dry deposition of ammonia, nitric acid, ammonium and nitrate to the Tampa Bay Estuary, FL, USA. *Atmos. Environ.* 35, 3947–3955.
- Reynolds, M.R., 2000. Prediction of particle deposition on to rough surfaces. *Agric. For. Meteorol.* 104, 107–118.
- Ross, C.A., Jarvis, S.C., 2001. Development of a novel method to measure NH₃ fluxes from grass swards in a controlled laboratory environment (a mini-tunnel system). *Plant and Soil* 228 (2), 213–221.
- Sauer, T.J., Norman, J.M., 1995. Simulated canopy microclimate using estimated below canopy soil surface transfer coefficients. *Agric. For. Meteorol.* 75, 135–160.
- Schjoerring, J.K., Husted, S., Mattson, M.E., 1998. Physiological parameters controlling plant-atmosphere ammonia exchange. *Atmos. Environ.* 32 (3), 491–498.
- Shaw, R.H., Periera, A., 1982. Aerodynamic roughness of a plant canopy: a numerical experiment. *Agric. Meteorol.* 26, 51–65.
- Shuttleworth, W.J., 1988. Corrections for the effect of background concentration change and sensor drift in real-time eddy correlation systems. *Bound.-Lay. Meteorol.* 42, 167–180.

- Sievering, H., 1986. Gradient measurements of sulfur and soil mass dry deposition rates under clean air and high wind-speed conditions. *Atmos. Environ.* 20, 341–345.
- Smith, R.I., Fowler, D., Sutton, M.A., Flechard, C., Coyle, M., 2000. Regional estimation of pollutant gas dry deposition in the UK: model description, sensitivity analyses and outputs. *Atmos. Environ.* 34, 3757–3777.
- Sutton, M.A., Burkhardt, J.K., Guerin, D., Nemitz, E., Fowler, D., 1998. Development of resistance models to describe measurement of bi-directional ammonia surface–atmosphere exchange. *Atmos. Environ.* 32 (3), 473–480.
- Weber, R.J., Orsini, D., Daun, Y., Lee, Y.-N., Klotz, P.J., Brechtel, F., 2001. A particle-into-liquid collector for rapid measurement of aerosol bulk chemical composition. *Aerosol Sci. Technol.* 35, 718–727.
- Wesely, M.L., 1989. Parameterization of the surface resistance to gaseous dry deposition in regional-scale numerical models. *Atmos. Environ.* 23 (6), 1293–1304.
- Wesely, M.L., Cook, D.R., Hart, R.L., 1985. Measurements and parameterization of particulate sulfur deposition over grass. *J. Geophys. Res.* 90, 2131–2143.
- Wesely, M.L., Hicks, B.B., 2000. A review of the current status of knowledge on dry deposition. *Atmos. Environ.* 34, 2261–2282.
- Wilson, J.D., Catchpoole, V.R., Denmead, O.T., Thurtell, G.W., 1983. Verification of a simple micrometeorological method for estimating the rate of gaseous mass transfer from the ground to the atmosphere. *Agric. Meteorol.* 29, 183–189.
- Yamulki, S., Harrison, R.M., 1996. Ammonia surface-exchange above an agricultural field in southeast England. *Atmos. Environ.* 30, 109–118.
- Zhu, T., Pattey, E., Desjardins, R.L., 2000. Relaxed eddy-accumulation technique for measuring ammonia volatilization. *Environ. Sci. Technol.* 34, 199–203.
- Zunckel, M., 1999. Dry deposition of sulphur over eastern South Africa. *Atmos. Environ.* 33, 3515–3529.